

RATE DETERMINING STEPS STUDY IN CADMIUM SORPTION FROM AQUEOUS SOLUTIONS BY SUNFLOWER LEAVES

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ABSTRACT

Batch studies of cadmium ion sorption by dried sunflower leaves were carried out to identify the main rate controlling steps in the overall uptake mechanism, using a single external mass transfer diffusion model and intraparticle mass transfer diffusion model. Many classical parameters influencing cadmium sorption mechanisms namely: initial cadmium concentration, agitation speed, initial solution pH, particle size, temperature, sorbent mass and cadmium salt nature were investigated. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients by separating the two mechanisms, based on the adequacy of correspondence models with experimental data of these parameters. The process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Analysis of mechanistic steps involved in the sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied.

Keywords: Sorption; Cadmium; Dried sunflower leaves; External film mass transfer; Intraparticle diffusion

INTRODUCTION

In the field of environmental pollution there are few subjects that, during recent years, have been developed as rapidly as the study of toxic metals. The contamination of water by toxic heavy metals is a world-wide environmental problem. Cadmium, in particular, has received a great deal of attention due to its highly toxic nature and its tendency to accumulate in the tissues of living organisms (Friberg et al. [1]). The main sources of cadmium in streams are effluents from industries such as electroplating, smelting, paints, plastics, battery, zinc mining and refining (Chong and Volesky [2]). Because of its high toxicity, most countries include cadmium among the “priority pollutants” requiring suitable treatment prior to discharge into the environment (Puranik et al. [3], Butter et al. [4]). At present, a variety of physicochemical processes are employed to treat cadmium-containing effluents. These processes, however, prove expensive when situations involving high volume and low metal concentration

(typically less than 50 mg/L) are encountered (Puranik et al. [3]). Methods such as chemical precipitation and reverse osmosis, as examples, result in incomplete metal removal, have high reagent or energy requirements, and generate toxic sludge which are difficult to dewater and other waste products that require careful disposal (Peters et al. [5], Brierley et al. [6]). Increasing awareness of the environmental impact of metal ions in our water systems has encouraged interest in novel adsorption systems. Recently, considerable research has involved materials of biological origin and many forms of biomass have been shown to be effective metals sorbents. Dried sunflower leaves as a waste can be an alternative and favourable sorbent material for pollutants such heavy metals. The sorption kinetics of cadmium from aqueous solution by dried sunflower leaves has been studied (Benaïssa and Elouchdi [7]), however, no information are available for its kinetics controlling mechanisms in the literature. Determination of the rate limiting steps in sorption is necessary in order to define the rate parameters for design purposes (Sag and Aktay [8]). For solid-liquid sorption process, the solute transfer process was usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

As a continuation of our previous work (Benaïssa and Elouchdi [7]), the aim of this work is the study of kinetics controlling mechanisms of cadmium sorption by dried sunflower leaves in batch conditions: external mass transfer and intraparticle diffusion. External and intraparticle diffusion models were separately examined according to the main sorption parameters studied such as: initial cadmium concentration, agitation speed, initial solution pH, particle size, temperature, sorbent mass and cadmium salt nature. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients, based on the adequacy of correspondence models with experimental data of these parameters.

TRANSFER DIFFUSION MODELS

The sorption of solute on solid particles has been extensively studied. It is generally agreed that there are four consecutive steps which describe the overall sorption process of sorption from a solution by a sorbent particle (Furusawa and Smith [9]). These steps, as adapted to apply to the sorption of metal ions by a sorbent particle, are as follows:

- 1- External mass transfer of the metal ions from the solution bulk to the boundary film;
- 2- Metal ions transport from the boundary film to the surface of the sorbent particle;
- 3- Diffusion of the metal ions within the sorbent particle to the sorption sites: internal diffusion of metal ions;
- 4- Final uptake of metal ions at the sorption sites, via complexation, sorption, or precipitation, which is fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the

agitation given to the solution (400 rpm) is considered as sufficient (Benaïssa and Elouchdi [7]) to avoid steps 1 and 2 being controlling steps. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag and Aktay [8]). In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al. [10]): sorption is a quasi-instantaneous process, as well as complexation mechanism, precipitation seems to occur with a lower rate (Tsezos and Volesky [11]). The sorption rate will be controlled by the rate of diffusion (Peniche-Covas et al. [12]). Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. Models were established to determine the two coefficients initially based on single resistance mass transport analysis (McKay et al. [13]).

1- External mass transfer resistance model

This model assumes that the surface concentration of solute, C_s , on the sorbent is negligible at $t = 0$, and that intraparticle diffusion is also negligible; it is applied to calculate the initial rate of metal sorption (McKay and Poots [14]). The initial rate of sorption can be determined using the classic mass transfer equation (1) which describes the evolution of metal ion concentration C_t in solution:

$$dC_t/dt = -\beta_L S (C_t - C_s) \quad (1)$$

where β_L is the external mass transfer coefficient, C_t the liquid phase solid concentration at a time t , C_s the liquid phase solute concentration at the particle surface and S the specific surface area for mass transfer.

This equation can be simplified, by substituting the following boundary conditions: $C_t \rightarrow C_0$ and $C_s \rightarrow 0$ when $t \rightarrow 0$; C_0 = initial metal ion concentration (McKay et al. [13], McKay and Poots [14], Weber and Morris [15]) to:

$$d(C_t/C_0)/dt = -\beta_L S \quad (2)$$

So the external mass transfer rate, $\beta_L S$, is approximated by the initial slope of the C_t/C_0 vs. time graph and can be calculated either by assuming a polynomial relation between C_t/C_0 and time or based on the assumption that the relation-ship was linear for the first initial rapid phase. The first technique was used here.

2- Intraparticle diffusion resistance model

Weber and Morris [15] demonstrated that in intraparticle diffusion studies, rate processes are usually expressed in terms of square root of time. So q_t or fraction metal sorbed is plotted against $t^{0.5}$ as follow:

$$q_t = k t^{0.5} \quad (3)$$

where: q_t is the solute concentration in the solid and k the slope of the plot. If particle diffusion is rate controlling, the plots q_t versus $t^{0.5}$ are linear and the slope of the plots is defined as an intraparticle diffusion rate parameter (McKay et al. [13]). In theory, the plot between q_t and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore (Ho and McKay [16]).

MATERIALS AND METHODS

1- Sorbent material and metal

In this work, an agricultural waste: dried sunflower leaves were used as an alternative low-cost sorbent in the removal of cadmium from aqueous solutions. It was collected in autumn 2001 from the region of Amieur, in Tlemcen-Algeria, in the form of large dried flakes. It was used as a sorbent material after the following treatment: 10 g of the sorbent material were contacted with 2 L of distilled water in a beaker agitated vigorously (400 rpm) by a magnetic stirrer at ambient temperature of 25°C during 4 h, then continuously washed with distilled water to remove the surface adhered particles and water soluble materials, and oven-dried overnight at 80°C for 24 h after filtration. This material was crushed and sieved to have particles of size: 0.50 – 3.15 mm for further batch sorption experiments.

Cadmium solutions of desired concentration were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Windor Laboratories Limited), by dissolving the exact quantities of cadmium salts in distilled water. All chemicals were commercial products used without purification.

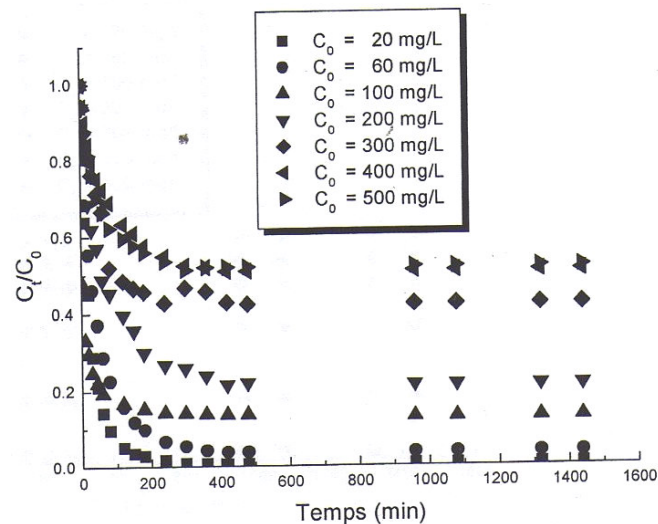
2- Uptake kinetics

The experimental systems and procedures have been described elsewhere (Benaïssa and Elouchdi [7]).

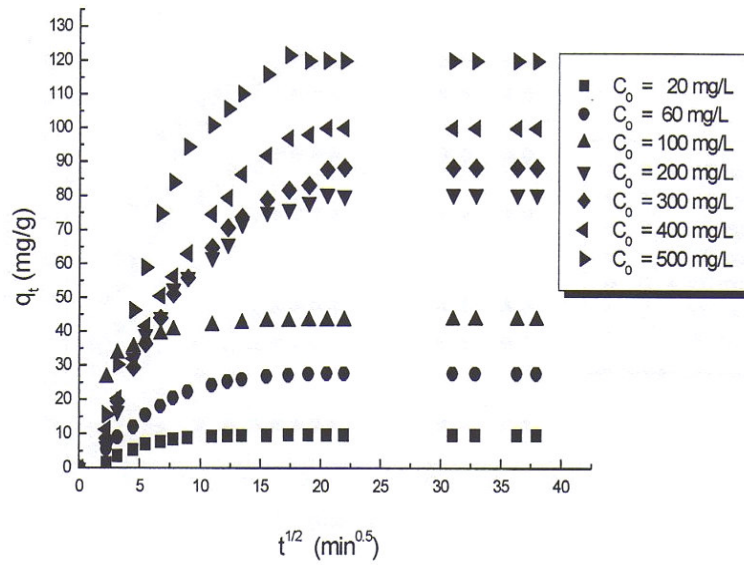
RESULTS AND DISCUSSION

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during metal sorption, described by external mass transfer (boundary layer diffusion) and intraparticle diffusion. Figures 1a, b and c (as a typical example) show plots of C_t / C_o versus time, q_t versus $t^{0.5}$ and Bt versus t for the effect of initial cadmium concentration on cadmium sorption by dried sunflower leaves. Table 1 summarises the mass transfer coefficients for the different kinds of transfer resistance.

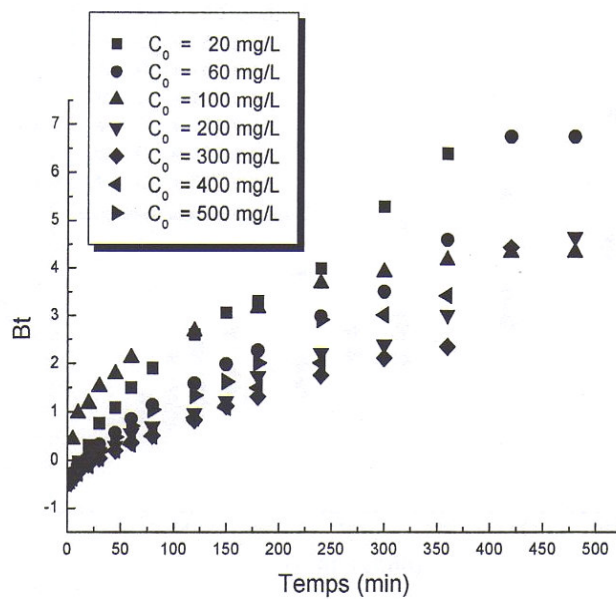
As shown in Table 1, the values of mass transfer coefficients obtained are different and dependent on the experimental parameter studies. In Figure 1b (as a typical example) showing q versus $t^{0.5}$, three linear regions were observed in the same experiment. McKay et al. [13] explains a non linear plot by a variety of intraparticle diffusion resistance mechanisms, depending on diffusion through pores of various sizes. The complex nature of the curve reflects the two-stage external mass transfer followed by intraparticle diffusion of cadmium ions onto dried sunflower leaves particles. The slope of the third linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, C (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect (Kumar et al. [17]). For all experimental parameters studied, a positive and significant ordinate intercepts, C (mg/g), is obtained indicating the influence of external rate control (Slag and Aktay [8]).



(a)



(b)



(c)

Figure 1: Effect of initial cadmium concentration on cadmium sorption kinetics by dried sunflower leaves. (Sorbent dose= 2 g L⁻¹; natural initial solution pH, agitation speed = 400 rpm; particle size = 0.125 – 1.60 mm, T = 25°C)
 (a) C_t/C_0 versus t , (b) q versus $t^{0.5}$ and (c) Bt versus t

Table 1: Effect of different experimental parameters on diffusion coefficients for cadmium ion sorption by dried sunflower leaves

	External mass transfer $\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$	Intraparticle diffusion $k \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$ $C \text{ (mg/g)}$		Boyd model $B \cdot 10^3 \text{ (min}^{-1}\text{)}$	R^2
C_0 (mg/L) Initial cadmium concentration					
20	35.93	0.07	8.59	17.94	0.9756
60	34.50	0.17	24.16	14.58	0.9803
100	54.56	0.33	37.91	8.56	0.8393
200	19.32	1.15	56.62	9.79	0.9833
300	9.81	1.54	54.85	9.34	0.9410
400	8.36	1.55	68.58	10.59	0.9933
500	11.55	3.29	65.16	13.33	0.9814
m (g) Sorbent dose					
0.3	37.25	0.67	62.04	12.58	0.9520
0.6	54.56	0.33	37.91	8.56	0.8393
1.2	161.76	0.03	24.13	20.89	0.9026
1.8	213.06	0.20	14.23	30.63	0.8481
N (rpm) Agitation speed					
250	68.00	1.69	29.37	29.34	0.8425
400	96.65	0.33	37.91	8.56	0.8393
500	43.00	0.38	34.16	16.03	0.8891
700	39.80	0.29	33.76	21.12	0.8666
900	28.67	0.47	30.49	23.96	0.9512
T (K) Temperature					
10	17.86	0.54	34.39	12.48	0.9901
20	19.81	0.31	36.96	13.19	0.9884
25	54.56	0.33	37.91	8.56	0.8393
40	30.72	0.44	35.05	12.94	0.9744
pH_0 Initial pH of solution					
3	20.40	0.47	30.38	10.61	0.9837
4	26.10	0.53	34.41	10.75	0.9836
5	22.55	0.46	34.83	10.81	0.9839

6	30.57	0.49	36.98	10.94	0.9520
7	21.76	0.60	33.73	11.06	0.9743
7.5	28.46	0.60	34.53	9.98	0.9779
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dp(mm)		Particle size			
<hr/>					
0.5-1	27.84	0.38	41.73	13.00	0.9612
1-1.25	24.10	0.34	40.61	16.10	0.9514
1.25-3.15	21.26	0.76	31.15	11.94	0.9844
> 3.15	13.19	0.97	23.44	10.29	0.9848
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Salt		Cadmium salt nature			
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Cd acetate	90.42	0.36	41.33	23.17	0.9764
Cd nitrate	44.00	0.33	37.91	15.55	0.9201
Cd carbonate	89.58	0.22	47.01	35.76	0.8271
Cd sulphate	110.28	0.18	47.34	17.74	0.8844

1- Effect of initial cadmium concentration: From results obtained, except for some points, the external film mass transfer coefficient ($\beta_L S$) generally decreases as the initial cadmium concentration increases. This result is not consistent with the fact external transport can become the rate-limiting step in systems, which have a dilute concentration of solute (Sag and Aktay [8]). Both the rate of sorption, described as the slope of the plot of the amount of metal sorbed as a function of $t^{0.5}$ and the ordinate intercept increases with initial cadmium concentration.

2- Effect of agitation: Agitation plays an important role in external mass transfer and as result; its influence is restricted to kinetic studies (Saucedo et al. [18]). Agitation influences the distribution of the solute in the bulk solution but can also act on the formation of the external boundary film. Increasing the agitation speed from 250 to 400 rpm increased the $\beta_L S$ value; this was expected as increased turbulence reduces the film boundary layer surrounding the sorbent particle. Increasing the agitation speed beyond 400 rpm, however, decreased the $\beta_L S$ value, indicating that external film mass transfer was not the rate-limiting step in a well-agitated vessel. Comparison of intraparticle diffusion coefficients determined for different agitation speeds showed that variation of agitation had little effect on both the internal diffusion rate k value and the thickness of the film boundary layer surrounding the sorbent particle. This was expected as agitation only influences the external transport step. The slight effect of agitation implies that external mass transfer is not the sole rate-limiting phase, and confirms that intraparticle diffusion resistance needs to be included in the analysis of overall sorption. These deviations from the models also indicate that single models are not sufficient to describe experimental points accurately (Sag and Aktay [8]).

Experiments with a low agitator speed result in a non-uniform distribution of the sorbent through the solution. External mass transfer and bulk mass transfer therefore have a limited effect on this sorption rate (Guibal et al. [19]). Increasing the degree of agitation increased turbulence that reduces the film boundary layer surrounding the sorbent particle. The results are in agreement with Helfferich, [20] who stated that external transport is the rate limiting step in systems which have (a) poor mixing (b) dilute concentrate of sorbate (c) small particle sizes of sorbent and (d) high affinity of sorbate for sorbent.

3- Effect of particle size: Particle size plays an important part in the resistance of the film to diffusion, relating respectively to contact surface (Saucedo et al. [21]). As shown in Table 1, particle size influences the sorption rate. As the particle size decreases, the external surface of the sorbent particles increases. The initial external diffusion rate ($\beta_L S$) increases by lowering the particle size of the sorbent. Under the same conditions, the intraparticle diffusion rate k decreases. This was expected since a decrease in the particle size decreases both the intraparticle diffusion resistance and the external mass transfer resistance. Increasing the particle size resulted in a greater time to diffuse to the interior of the particle. The increased particle size will introduce a higher intraparticle resistance and will therefore have a lower internal diffusion coefficient. If the intraparticle diffusion mechanism plays an important part in the control of metal sorption, increasing particle will result in a decrease in sorption rate; the metal ion will therefore have a greater intraparticle distance to diffuse before the sorbent becomes saturated (Guibal et al. [19]). Consequently increasing particle size increases the time needed to reach equilibrium.

4- Effect of temperature: The results obtained here demonstrate that temperature is a parameter which affects the sorption kinetics, within the temperature range studied. An increase in temperature (10-25°C) is followed by an increase in the values of $\beta_L S$, k and the thickness of the film boundary layer surrounding the sorbent particle. In general, an increase in temperature is followed by an increase in the diffusivity of the ion, and consequently by an increase in the sorption rate if diffusion is the rate controlling step.

5- Effect of sorbent mass: The results obtained shows that $\beta_L S$, the external mass transfer coefficient, strongly increases with dried sunflower leaves mass, while both the intraparticle mass-transfer coefficient k and the thickness of the film boundary layer surrounding the sorbent particle decrease. These observations suggest that the cadmium sorption kinetics by dried sunflower leaves is largely determined by intraparticle diffusion steps.

6- Effect of initial pH of solution: Solution pH plays an important part in the controlling the rate of sorption. This influence is related to the rearrangement and the ionic size of metal species in the solution influencing the diffusion through the sorbent structure (Guibal et al. [19]). As shown in Table 1, except some points, as the initial pH of solution increases in the range 3-6, both the particle mass-transfer coefficient k and the thickness of the film boundary layer surrounding the sorbent particle slightly

increases (not clear). The value of β_{LS} also increases. Beyond pH 6, no clear tendency is observed about these diffusion coefficients. The results are expected because increasing the initial pH solution results in the formation of cadmium hydroxides (pH = 7 - 7.5) and the diffusion through almond peel is reduced as a result of its larger ionic size.

7- Effect of cadmium salt: The results presented in Table 1, show that the nature of cadmium salt used is a parameter which affects the sorption kinetics. Values of both β_{LS} and k_i values are cadmium salt nature dependent.

As the complex nature of the intraparticle diffusion plot, the sorption process is found to be of a complex nature. Thus in order to characterize what the actual rate-controlling step involved in cadmium ions sorption process is, the sorption data were further analysed by the kinetic expression given by Boyd et al. [22].

$$F = 1 - (6/\pi^2) \exp(-Bt) \quad (4)$$

where F is the fraction of solute sorbed at different times t and Bt is a mathematical function of F and given by:

$$F = q_t/q_\infty \quad (5)$$

where, q_t and q_∞ represents the amount sorbed (mg/g) at any time t and at infinite time (in the present study 3-7 h depending on the experimental parameter studied (Benaïssa, and Elouchdi [7])

Substituting Eq. (4) into Eq. (5), the kinetic expression becomes:

$$Bt = -0.4967 - \ln(1 - q_t/q_\infty) \quad (6)$$

Thus the value of Bt can be calculated for each value of F using Eq. (6) and plotted against time. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption (Kumar et al. [17]). From Fig. 1c (as a typical example), it was observed that the plots were linear but did not pass through the origin, indicating that, for the all experimental parameters studied here, external mass transport mainly governs the rate-limiting process (Boyd et al. [22]).

CONCLUSIONS

Analysis of diffusion mechanisms of cadmium sorption by almond peel was problematic. Diffusion mechanisms were predominant in rate controlling steps. Three models of transfer control were examined: external mass transfer, via a film resistance, the intraparticle diffusion model and Boyd model. These models were not easily applied to evaluate variations in rates and diffusivities. The investigated operating

parameters have different effects on mass transfer coefficients. Under our experimental conditions, the analysis of mechanistic steps involved in the cadmium sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages.

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